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The Analysis of Vibrational Spectra of Species Adsorbed at the Electrode
Solution Interface. A Theoretical Model for the Effects of
Potential on the Observed Spectra

by

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Short communication

THE ANALYSIS OF VIBRATIONAL SPECTRA OF SPECIES ADSORBED AT THE ELECTRODE-SOLUTION INTERFACE

A THEORETICAL MODEL FOR THE EFFECTS OF POTENTIAL ON THE OBSERVED SPECTRA

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Interactions of electroactive species and adsorbates with the solvent, electrolyte, and electrode are observed in the in situ infrared spectrum of the interface {3-5}. The analysis of these spectra is usually difficult, and conventional normal coordinate analysis, while useful for simple molecular systems which are undisturbed by the environment, is not well suited for systems whose vibrational structure is perturbed by external forces. We have recently formulated a Taylor series in symmetry-adaptable spherical harmonic functions [6] which has been applied successfully to account for spectral perturbations observed in an electrochemical system.

In the method, an adsorbed molecule is described as the sum of pair-wise potential energy functions which operate between the bonded and non-bonded atoms. Perturbations are introduced by additional pair-wise terms operating between the perturbing force center and the specific atoms in the molecule. In many systems, Morse or Lennard-Jones potential energy functions may be used. Cartesian force constants, from which the vibrations of the system are determined, are calculated from expansion of the pair-wise potential functions to second order using the symmetry-adapted form of the Taylor series. The elements of the cartesian force constant matrix have been derived for the general case. The form of the diagonal elements are given by

$$k_{ii} = \frac{1}{2} (4\pi)^{1/2} [I_{20}(R) + (2X_i^2 - X_j^2 - X_k^2) I_{22}(R)/R^2] \quad (1)$$

* To whom correspondence should be addressed.

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eliminate $(4\pi)^{1/2}$

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where X_i is the i th cartesian component ($i = x, y, z$) of the vector R between the atomic centers. The off-diagonal elements are given by

$$k_{ij} = \cancel{X_i X_j} I_{22}(R) / R^2 \quad (2)$$

The radial quantities in these expressions, $I_{20}(R)$ and $I_{22}(R)$, are specifically

$$I_{20}(R) = \frac{2}{R} \frac{dg}{dR} + \frac{d^2g}{dR^2} \cancel{(4\pi)^{-1/2}} \quad (3)$$

and

$$I_{22}(R) = \frac{d^2g}{dR^2} - \frac{1}{R} \frac{dg}{dR} \cancel{(4\pi)^{-1/2}} \quad (4)$$

where g is the potential energy function which operates between the two atomic centers. Following construction of the force constant matrix, the vibrational frequencies are obtained directly. A description of the expansion and its application in modeling solvent perturbations has been given in detail [7-19].

We apply the model to the problem of the analysis of the potential dependent vibrational frequency shift of carbon monoxide adsorbed on platinum electrodes. When CO is adsorbed on polycrystalline platinum electrodes from aqueous acid solution, a band is observed at about 2070 cm^{-1} . This band has been assigned to CO linearly bonded to an on-top site on the platinum surface. As the potential is made more positive the frequency of the band shifts to higher wavenumber. For a saturation coverage of carbon monoxide the shift is linear with a slope of about $30 \text{ cm}^{-1}/V$ [20-24]. The nature of this shift has been attributed to chemical bonding interactions with the metal [22,25] and interactions with the electric field across the electric double layer [26-28].

The potential energy is developed as the sum of pair-wise interactions for the various atoms in the system. Specifically:

$$V = V_{CO} + V_{CS} + V_{OS} \quad (5)$$

In this expression, V_{CO} is a Morse potential which represents the bonding in carbon monoxide,

$$V_{CO} = D \exp[a(r_{CO}^0 - r_{CO})] \{ \exp[a(r_{CO}^0 - r_{CO})] - 2 \} \quad (6)$$

The values of the dissociation energy (D), Morse parameter (a), and equilibrium C-O bond distance (r_{CO}^0) were arbitrarily chosen to be those for gas-phase carbon monoxide; r_{CO} is the carbon-oxygen separation. The function V_{CS} describes the interaction of carbon with the surface. The model of the platinum surface consisted of 14 platinum atoms arranged in a (111) configuration. A Lennard-Jones potential was chosen for the interaction of the carbon atom with each of the surface atoms, so V_{CS} is the sum

$$V_{CS} = \epsilon \sum_i (c/r_{ci})^6 \{ (c/r_{ci})^6 - 2 \} \quad (7)$$

The parameters ϵ and c represent the dissociation energy and equilibrium carbon-platinum bond distance respectively. The radii r_{ci} are the distances between



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the carbon atom and each platinum atom i . The last term in the potential, V_{OS} , represents the oxygen-surface platinum interaction. In this interaction,

$$V_{OS} = \sum_i D' \exp[\gamma(r_{oi}^o - r_{oi})] \{ \exp[\gamma(r_{oi}^o - r_{oi})] - 2 \} \quad (8)$$

in which the r_{oi} are the distances between the oxygen and each platinum atom. The other parameters have their usual meaning in the Morse potential.

The parameters in the expression for the interaction potential are listed in Table 1. The parameter r_{oi}^o in V_{OS} was chosen to make this a repulsive term; the remaining parameters in V_{CS} and V_{OS} were optimized by a least-squares fit to the experimental binding energies and the carbon-oxygen and platinum-carbon vibrational frequencies as found under uhv conditions for carbon monoxide bonded both to on-top and bridging sites. Complete C-O and Pt-C bond length optimizations were performed at each site by the Newton-Raphson method. The geometry was optimized with carbon monoxide bound normal to the surface, with the carbon end towards the metal. The parameters in the V_{CS} and V_{OS} parts of the potential were refined until the calculated binding energy and vibrational frequencies gave acceptable agreement with experiment.

The chemical bonding mechanism was simulated by varying the CO-platinum surface binding energy, as it has been suggested that the binding energy changes with electrode potential [29]. The binding energy, calculated as the difference between the total energy from eqn. (5) and the dissociation energy of isolated carbon monoxide, was varied by changing the values of the dissociation energy for the oxygen-surface and carbon-surface interactions (D' and ϵ). Assuming that the binding energies of the surface-adsorbate interactions vary linearly with potential, we calculate that the CO vibrational frequency shifts linearly (Fig. 1).

The suggestion has also been made that a pure electric field type mechanism (Stark effect) may operate to produce the observed potential dependent spectral shift [27]. An electric field perturbation of this type was modeled by adding the new quantity V_{field} to the interaction potential:

$$V_{field} = E_z M(z^o - z) \quad (9)$$

A potential of this type is consistent with the Gouy-Chapman-Stern theory of the electrical double layer [30]. In this expression E_z is the electric field strength in a

TABLE 1
Parameters in the interaction potential

| | | |
|----------|--|-------------------------------|
| V_{CO} | $D = 11.11 \text{ eV}$ $a = 23.1 \text{ nm}^{-1}$ | $r_{CO}^o = 0.113 \text{ nm}$ |
| V_{CS} | $\epsilon = 2.04 \text{ eV}$ $c = 0.181 \text{ nm}$ | |
| V_{OS} | $D' = 0.13 \text{ eV}$ $\gamma = 8.6 \text{ nm}^{-1}$ | $r_{oi}^o = 0.46 \text{ nm}$ |

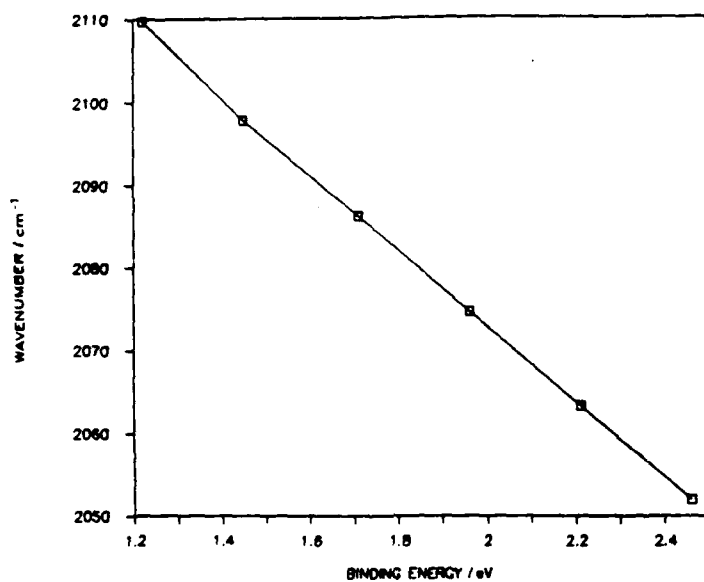


Fig. 1. Plot of the C-O stretching frequency of carbon monoxide versus the binding energy which acts between carbon monoxide and the platinum surface.

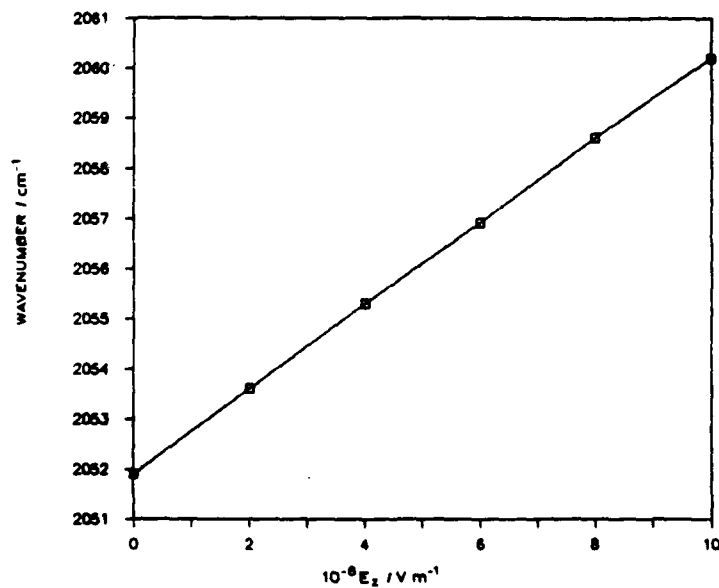


Fig. 2. Plot of the carbon monoxide C-O stretching frequency versus the applied electric field strength.

direction normal to the surface, M is $(d\mu/dz)$ obtained from expansion of the dipole moment function, and the term $(z^\circ - z)$ is the relative displacement of the atom from its equilibrium position (z°) in a direction normal to the surface. The experimental value of $(d\mu/dz)$ for CO in gas phase is 3.093 D/\AA [31]. Lambert has found that this value increases by about a factor of 2 when CO is adsorbed on Ni (110) [26]. Therefore, to calculate the electric field perturbation, $(d\mu/dz)$ was taken to be 6.18 D/\AA . Using this model, a Stark tuning rate of $9.0 \times 10^9 \text{ cm}^{-1}/\text{V m}^{-1}$ was calculated which is precisely the experimental gas-phase value [26]. The corresponding predicted variation of the CO stretching frequency with electric field strength is shown in Fig. 2.

It is concluded that because an electric field at an electrode depends upon the accumulation of charge on the surfaces of the conductors, it is difficult to separate electric field perturbations from the changes in chemical bonding between the adsorbate and the metal. The present analysis predicts that the observed spectral shifts are accounted for by a combination of chemical bonding and electric field interactions. The model provides an excellent analysis of the vibrational structure of the interface under potential perturbations.

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